STUDY OF THE SOLIDS OF SKIMMED MILK

BY

J. A. WHITTINGTON
L. T. WILSON
WM. YONKMAN

ARMOUR INSTITUTE OF TECHNOLOGY

1914

543.2
W61

Illinois Institute
of Technology
UNIVERSITY LIBRARIES

AT 353
Whittington, J. A.
A technical study of the
solids of skimmed milk

For Use In Library Only

A THECNICAL STUDY OF THE SOLIDS OF SKIMMED MILK.

A THESIS

Presented By

J. A. Whittington

Lester T. Wilson

Wm. Yonkman

To The

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

For The Degree

Of

BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

Having Completed The Prescribed Course

In

Chemical Engineering.

1914.

Approved.

P. M. McConnack
Prof. of Chem. Engineering
L. M. Raymond
L. C. Morrin

ILLINOIS INSTITUTE OF TECHNOLOGY
PAUL V. GALVIN LIBRARY
35 WEST 33RD STREET
CHICAGO, IL 60616

543.2
W61

Contents.

I. Introduction.

(a) Outline of properties of the solids of skimmed milk.

(b) Technical uses of the solids of skimmed milk.

(c) The commercial status of the skimmed milk problem.

II. Experimental Work.

(a) Method of Analysis.

(b) The yield of casein as influenced by the use of different precipitants.

(c) The rate and quality of lactose conversion by fermentation with a lactic acid culture.

(d) The influence of lime on the increase in yield of lactic acid.

(e) The effect of removing the protein from skimmed milk upon the rate of conversion Of lactose to lactic acid.

(f) The recovery of milk sugar.

(g) The recovery of lactic acid.

III. Conclusion.

IV. Bibliography.

24864

Introduction.

Skim milk is that portion of the "whole milk" left after the butter fat has been removed by skimming or more economically by the centrifugal method.

An average analysis of milk received from a source of known purity and from which the skim milk used in this work was subsequently taken is as follows:

Fat	3.4 %
Casein	3.2 %
Albumin	0.6 %
Lacto-protein	0.1 %
Lactose	4.5 %
Ash	0.7 %
Water(by difference)	87.5 %
	100.0 %

It will be readily seen that other materials more or less valuable remain in the skim milk after the fat has been removed, and it is a study of this residue with which this thesis is concerned.

An analysis of the skim milk received is as follows:-

Total solids	9.63 %
Water (by difference)	90.37 %

An analysis of this milk for solids gave:-

Casein	3.58 %
Lactose	4.65 %
Albumin	0.70 %
Ash	0.67 %
Fat	0.15 %
	9.75 %

A Brief Description of the Solids.

1. Casein.

Casein is the chief characteristic protein substance found in milk. Because of a lack of uniformity in casein from different sources an exact structural formula cannot be written; however it can be considered a combination of alpha-amino acids and their derivatives. The casein of cows milk according to Hoppe-Seyler, has a percentage composition as follows:-

Carbon	52.92 %
Hydrogen	7.04 % to 7.53 %
Nitrogen	15.60 % to 15.91 %
Oxygen	22.78 %
Sulphur	0.75 % to 0.82 %
Phosphorous	0.80 % to 0.84 %

In milk casein is present as a calcium caseate and, on the authority Courant, not as the neutral salt but as a calcium dicaseate combined with calcium phosphate in such a manner as to give the well known collodal properties to the solids of milk.

Casein may be prepared commercially by precipitation with various acids such as sulphuric, hydrochloric, acetic, lactic and methyl or ethyl sulphuric acids.

Such salts as sodium chloride, magnesium, sulphate and sodium sulphate precipitate casein.

Rennet, a ferment obtained from the gastric mucosa of the calf, also precipitates casein but in a slightly modified form. Unlike the acid precipitated product that is obtained with rennet, called paracasein, it forms a calcium salt which is insoluble. Because of its ability to bring down casein without the use of acid, rennet finds its principle use in cheese making.

Alkaloids and the aniline dyes give complex insoluble compounds when added to skim milk.The product obtained with the pigments are of great

importance in the manufacture of casein paints.

Casein is readily soluble in dilute, aqueous, solution of the alkalies, the normal and acid carbonates of the alkalies and solution of the alkali earth compounds. Strong acids which do not decompose casein will dissolve it.

2. Milk Sugar or Lactose.

Lactose is the carbohydrate of milk. According to E. Fischer it is an anhydride of the following structural formula:-

CH OH(CHOH)

HC O.CH

O.OH(CHOH) CHOH.COH

The solution of lactose is dextro rotatory. The average normal specific rotation being 52.5 at a temperature between 15 and 25 degrees centigrade. It has a solution of nineteen parts per one hundred parts of water, and when separated from milk by evaporation comes down as white semi-transparant crystals.

3. Albumin.

The soluble albumin of milk resembles the albumin of white of egg and like it is precipitated by heating to 70 degrees centigrade.

4. Asn.

The ash remaining after milk nas been completely incinerated, consists according to analysis given by Leach, of the following inorganic salts:-

Total asn in sample	0.70 %
Potassium oxide	0.175 %
Calcium oxide	0.070 %
Magnesium oxide	0.140 %
Iron oxide	0.017 %
Sulphur tri-oxide	0.001 %
Phosphorous pent-oxide	0.027 %
Chlorine	0.100 %

Technical uses of the Solids of Skim Milk.

1. Casein.

The material as a cheese from the lactic or rennet fermentation of milk has been known since time immemorial, but its use in the arts and industries is of comparatively recent origin. While in the following list the main uses of casein are given it must be understood that they have not all been brought to technical perfection.

(a) As paper sizing.

Casein is dissolved in an alkaline solution

mixed with the filler and pigment to be used. The size is then spread on the uncallendered paper by means of small brushes. Used in this manner it gives a smooth even coat which is highly resistant.

(b) Casein Paint.

The agglutinant properties of a casein solution have already been mentioned. Excellent glues can be made by stirring up casein with distilled water to which has been added sodium bicarbonate and shellac. The advantage with casein glue lies in the fact that it can be used cold, thus avoiding the melting pot necessary to the utilization of common glue. By using formaldehyde in the glue a water proof and bacteria proof joint is obtained.

Plastic Masses.

When casein in alkaline solution is mixed with bone dust, powdered stone, etc., a mixture is obtained which becomes plastic on heating and thus may be presses and moulded.

By treating casein with formaldehyde a tough white product, which can be colored is obtained.

This material known as "Galalich" is used in making piano keys, insulating medium, billard balls and articles of like nature.

(d) Casein in the Textile Industries.

The gummy ammonical solution of casein is used as a medium for printing and fixing powdered pigments, which do not react with an alkali, to calico.

(e) Casein as a Food.

Casein in the form of cheese has an important position in the diet. The form which attracts the most attention because of the advertizing is that sold as the so-called nerve and brain food. Although there is justification for the use of these patent preparations the claims made for them and the prices charged are far out of proportion to the actual benefits derived from their use.

Lactose.

Since this compound is not fermentable by yeast it is placed in the wort and remains in the finished stout. The major part of the milk sugar finds a ready market as a medicine and for pharmaceutical preparations.

Albumin.

It is only when skim milk is heated about 70 degrees centigrade as in evaporation for the recovery of milk sugar that the albumin is precipitated. At present its only value is as cattle feed.

The Ash.

The ash has no commercial value.

Lactic Acid.

While lactic acid not naturally present in fresh milk it may be and is produced when milk undergoes natural fermentation. In such industries as butter making fermentation is allowed to proceed to an acid content of about 1% when the "ripened cream" is churned. Since the natural fermentation stops within certain limits the butter milk remaining after churning contains lactose as well as lactic acid. In the recovery of the milk sugar lactic acid would then be obtained as a by-product.

The straight preparation of lactic acid from skim milk is not feasible because of the ease with which a solution of cane sugar can be fermented

with suitable bacilli. This fermentation of sugar to lactic acid while proceeding readily stops at a given concentration. The increase of the yield of lactic acid from sugar solutions without the loss of an excess of the unconverted sugar presents a problem which was solved in this work.

Lactic acid is becoming commercially more important as its uses and properties are being investigated. It is used instead of the tartar bath in dyeing, as a mondant for wollen goods and at present is being substituted for the natural lactic acid occuring in beer, thus obviating the chance of contamination when ferments are added to produce the natural lactic acid.

Commercial Status of the Problem.

The profitable disposition of skim milk is a problem which the dairy interests are just beginning to study. In isolated creameries where the milk brought by the farmer is worked for its butter content alone the skim milk is usually fed to live stock. While this proceedure appears wasteful it is justified, because the limited capacity of the ordinary farmers creamery where milk is handled in such small quanities makes a profitable

production of casein, milk sugar and albumin impossible. However the tendency is toward large centralized creameries, handling from 1000 to 5000 gallons of whole milk per day.

Considering the creameries whose production of skimmed milk approximates 1000 gallons per day, and they are not uncommon, it will be seen that the handling of this bulk of heretofore almost waste material presents a serious problem.

The commercial market for such a material as casein, milk sugar, and crude albumin is at present well established, but because of superior knowledge and the necessity of making every item count, the bulk of these products come from European manufacturers. One of the largest butter making concerns in Chicago sell their curd to poultry raisers for chicken feed and a limited amount as cottage cheese. The manager of this creamery was of the opinion that the establishment of an industry for the commercial production of milk sugar was only a matter of a few years in which to conduct the necessary preliminary and experimental work.

Methods of Analysis.

Total Solids.

A clean aluminum disk is dried and weighed. A sample of milk is placed in the disk and the total quickly weighed. The disk is then placed on the water bath until it ceases to lose weight, when it is again rapidly weighed, to avoid the absorption of water.

$$\frac{\text{Loss in weight}}{\text{Weight of sample}} \times 100 = \% \text{ Solids.}$$

Casein.

Fifty c.c. of fresh skimmed milk is diluted to 250 c.c. and 75 c.c. of N/10 acetic acid slowly added, the mixture being continually and rapidly stirred during the addition. The precipitate is then washed by decantation, the washings being passes thru a quanitative filter paper and finally the precipitate is transfered to the filter. After draining for about an hour the precipitate and filter is transfered to a beaker and dissolved in exactly 100 c.c. of N/10 sodium hydroxide. The casein is completely dissolved and the paper transfered to a fine pulp. Complete solution

of the casein is attained in about ten minutes. The mixture is then filtered and the refractive index determined with the Pulfrich refractometer.

Since n for N/10 NaOH is 1.33444 at 20 degrees centigrade the results may be calculated as follows:-

Grams casein in 50 c.c. milk $\frac{N - 1.33444}{0.00152}$

Where the volume is 100 c.c. and the change of the index of refraction due to one gram of casein is 0.00152.

Milk Sugar.

The specific gravity of milk was determined with a delicate hydrometer, at a temperature of 20 degrees centigrade.

The quality of milk to be used for polarization varies with the specific gravity of the milk as shown by the following table:-

Sp. Gr.	Vol. of Milk to be used.
1.024	64.4 c.c.
1.026	64.3 c.c.
1.028	64.15 c.c.
1.030	64.00 c.c.
1.032	63.90 c.c.
1.034	63.80 c.c.
1.035	63.70 c.c.

N.B. This table applies only when the normal sucrose weight of the polariscope is 26.048 gm.

Place the quanity of milk indicated in the table in a flask graduated to 102.04 c.c. and add 1 c.c. of mercuric nitrate and 30 c.c. of mercuric iodide solution. Fill the flask to the mark with distilled water and shake well. The mixture is then filtered thru a dry paper(the first 10 c.c. being discard and the filtrate polarized. A ten centimeter tube is used and the scale reading gives the percent lactose direct.

Lactic Acid.

Lactic acid was determined by titrating 10 c.c. of sample with N/10 NaOH.

Experimental Work.

The casein was precipitated from skimmed milk by the use of the following precipitants:-

(1) Lactic acid - 4 % solution.

(2) Hydrochloric acid - 1 part con. HCl to 10 parts H O

(3) Sulphuric acid - 1½ parts by volume to 7 parts H O

(4) Acetic acid - 29 % solution.

(5) Ethyl sulphuric acid - 1 part con. H SO to 1 part alcohol.

(6) Methyl sulphuric acid - 1 part con. H_2SO_4 to 1 part methyl alcohol.

(7) Alums.

The following results were noted:-

Lactic acid - fine white curd - filtered fast.

Hydrochloric - fine curd - filtered fast.

Sulphuric - white curd coarser than above - filtered very slowly.

Acetic acid - white course curd - filtered slowly.

Ethyl sulphuric - white coarse curd - filtered very slowly.

Methyl sulphuric - slightly yellow curd - filtered very slowly.

The alums and $MgSO_4$ were not very satisfactory precipitants.

Weight of dried casein obtained from 3 # of skimmed milk with the different reagents. The skimmed milk contained 4.3 % casein.

Reagent	Wt. of Casein.
Lactic acid	.11 #
Hydrochloric acid	.11 #
Sulphuric acid	.12 #
Acetic acid	.10 #
Ethyl sulphuric acid	.11 #
Methyl sulphuric acid	.09 #

A can of milk (40 lbs.) was sterilized for 3-4 hours at a temperature of 170 F to 190 F; a ferment was added at 8:45 A.M., and the acidity of the milk was determined by titration with N/10 NaOH, the sugar content also being determined, the following data was ontained from which a curve was plotted.

Time	No.c.c. Titrated	No.c.c. N/10 NaOH used.	% Lactic Acid	%Lactose
8:45 A.M.	10	1.8	.163	4
9:45	10	2.1	.189	4
10:45	10	2.2	.198	4
11.:45	10	2.4	.216	3.97
12:45	10	2.5	.225	3.95
1:45 P.M.	10	2.8	.252	3.94
2:45	10	3.2	.278	3.90
3:45	10	3.7	.333	3.87
4:45	10	4.7	.423	3.75
7:45 A.M.	10	10.6	.954	3.06
8:45	10	10.2	.918	3.06
9:45	10	10.1	.909	3.06
10:45	10	10.1	.909	3.06
11:45	10	10.0	.900	3.06

Second run-culture added at 4:45 P.M.

Time	No. c.c. Titrated	No. c.c. N/10 NaOH used	% Lactic acid	% Lactose
8:30 A.M.	10	7.6	.684	3.5
9:30	10	8.6	.774	3.4
10:30	10	9.6	.860	3.3
11:30	10	9.4	.846	3.3
12:30	10	9.4	.846	3.3
1:30	10	9.4	.846	3.3

In order to increase the fermentation of the milk sugar to lactic acid, one meter of milk having a lactic acid content of 0.90 % was partially neutralized with 1000 c.c. N/20 Ca(OH) . The following results were obtained:-

Time Start	Total percent lactic acid.
8:20 A.M.	.950
9:20	1.330
10:20	1.620
11:20	1.780
12:20	1.890
1.20	1.890
1000 cc. N/20 Na(OH) was now added.	
2:00 P.M.	2.480
3:00	2.630
4.00	2.690
5:00	2.750
7:00 A.M.	3.02
12:00	3.24

The theory has been advanced that the protein of milk is necessary for lactic fermentation. To determine the effect upon the rate and quantity of milk sugar converted to acid when casein is removed the following experiment was undertaken.

The casein of a quart of skimmed milk was removed by precipitation with lactic acid and then a buttermilk culture was added to the whey, the following results were obtained:-

Time	No. cc. titrated	No.cc. N/10 NaOH used	% Lactic acid
9:30 A.M.	10	2.6	.234
10:30	10	2.6	.234
11:30	10	2.8	.252
12:30 P.M.	10	2.8	.252
1:30	10	2.7	.243
3:00	10	2.7	.243
4:00	10	2.7	.243
8:00 A.M.	10	2.8	.252
2:30 P.M.	10	3.9	.351
8:30 A.M.	10	6.0	.570
8:30 A.M.	10	7.8	.740
Monday after several days	10	10.8	.981

Recovery of Sugar.

The casein was precipitated from 40 lbs. of skimmed milk, containing 4.3 % sugar, with lactic acid, filtered, and the whey digested for some time with calcium carbonate and aluminium hydroxide. The insoluble matter was then filtered off and the filtrate concentrared in the vacuum evaporator to a syrup, which on standing gave crystals of lactose. During the concentration the albumen becomes insoluble which was filtered off before final concentration.

Yield.

1st crop 173 gm. - purity 97 % pure lactose 167.81 gm.
2nd " 357 " " 84 % " " 316.88
Total gms. pure lactose 384.69

453 x 40 x 4.3 % 736.16 gm. theoritical yield.

Therefore $\frac{384.69}{736.16}$ 52.5 % yield

One and fifty three hundredths pounds of dried casein was recovered, and during the concentration period .55 lbs. of crude albumen was thrown down.

The value of the products recovered is:-

Casein	$ 0.37	
Milk Sugar	.78	
Albumen	.02	
	$ 1.17	
Cost of raw material		$ .35
Cost of lime		.045
Cost of labor		.45
Int. Ins. Power depreciation		.16
		$ 1.005

The total profit per 40 lbs. of milk would then be 15.5 cents.

On a plant handling 1000 gallons per day this means a profit of #33.00 per day.

Recovery of Lactic Acid.

Forty pounds of milk, containing 4.5 % sugar, was allowed to stand several days - until the lactic acid content was 1.12 %.

The amount of lime required to neutralize the acid already formed, and also to neutralize all that will be formed, considering that all the milk sugar is converted to lactic acid, is calculated as follows:-

The formula for milk sugar is C H O H O

The formula for lactic acid is C H O

Therefore 1(C H O H O) 4(CH CH.OH.COOH)

2(CH CH.OH.COOH) CaO Ca(CH CH.OH.COO) H O

Therefore 1(C H O + H O) 2 CaO

453 x 40 x 4.5 % 815.4 gm. sugar.

Therefore 360: 112 :: 815.4 : x x 354

Therefore 354 gm. CaO was required to neutralize all the acid, but since the fermentation proceeds until an acid concentration of about one percent is reached, only 300 gm. of CaO was added.

The sugar was determined each day to determine the progress of the fermentation. When the percentage of sugar became very small the acidity of the milk was determined and found to be .72 %.

The calcium lactate was then decomposed by adding the calculated amount of H SO to react with the calcium lactate which was previously formed, to the solution, which was then heated and filtered.

The filtrate was concentrated in the vacuum evaporator to a syrup.

Yield:-

453 x 40 x 4.5% 815.4 gm. theoritical yield.

Actual yield 393.2 gm.

Therefore $\frac{393.2}{815.4}$ 48.3 % yield.

Conclusion.

Casein.

Casein of good marketable properties can be readily prepared from skimmed milk. A consideration of the yield and cheapness of the precipitant favors sulphuric acid as the reagent. The diversified uses of casein sometimes demand other precipitants, such as hydrochloric acid, acetic acid, etc., and it was found that the acids give results equal in all respects to the sulphuric acid product, always discounting the difference in initial cost of the above named acids over sulphuric acid.

When milk sugar as well as casein is to be recovered the organic acids or rennet are the only precipitating materials feasible, since the mineral acids would invert the milk sugar.

Milk Sugar.

This compound is readily recoverable from skimmed milk by methods which are comparatively simple, no expert knowledge and technique being required.

Lactic Acid.

The fermentation of sugar to lactic acid has a tendency to stop abruptly at about 1 % lactic acid. The reason for this straightening of the curve herin shown, is probably due to the toxic effect of this specific concentration of acid on the bacilli producing the fermentation.

By careful neutralization of the fermenting sugar as was done in this work the conversion may be carried to a point which is limited only by the amount of convertable sugar present.

The idea that the presence of milk protein is essential to the growth of the lactic acid bacilli is erroneous, although the conversion proceeds more slowly when casein has been removed.

Bibliography.

Scherer, Robt. The technical preparation and use of casein.

Rogers and Aubert. Industrial Chemistry.

Leach. Food Inspection and Analysis.

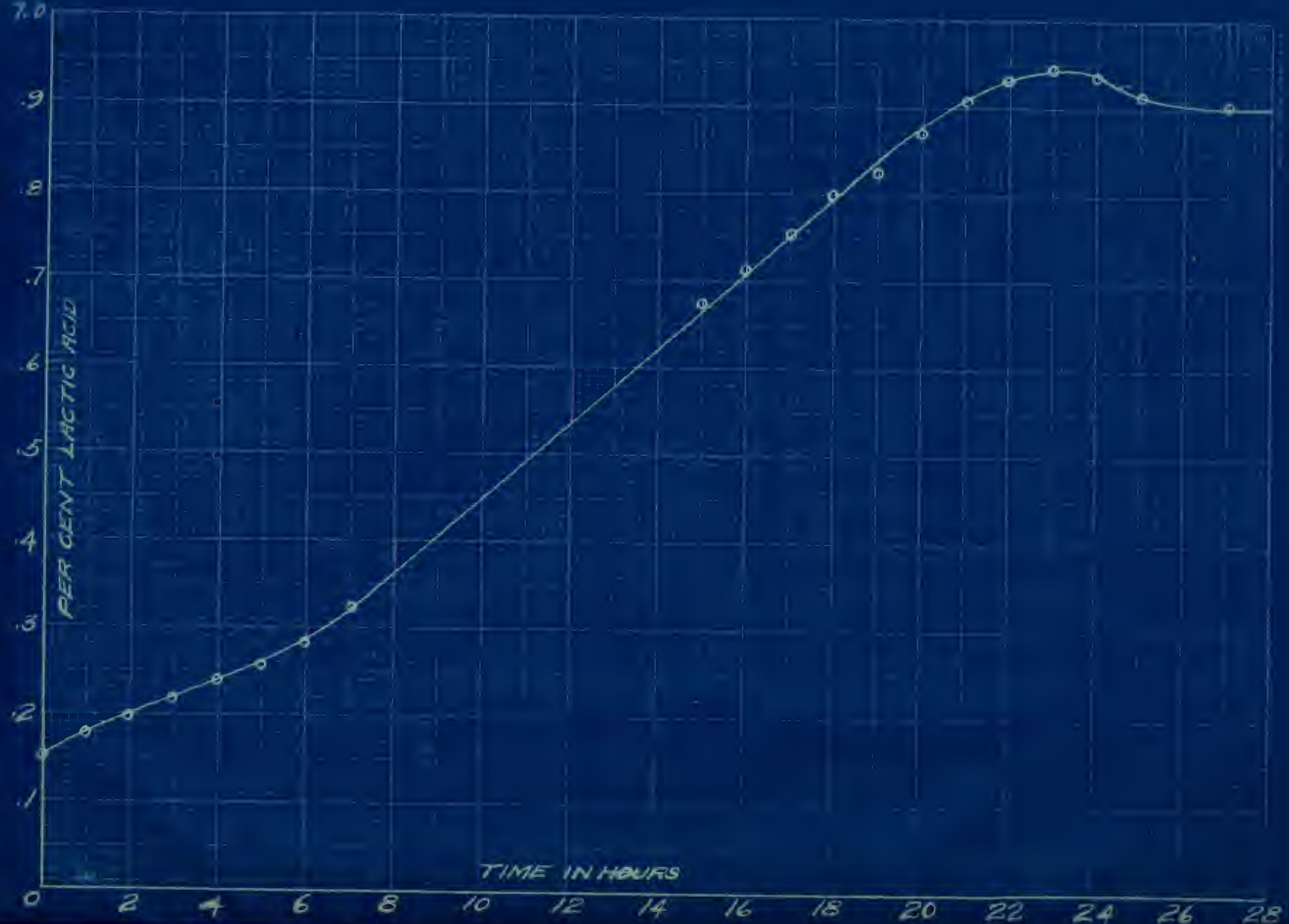
Thorpe. Dictionary of Applied Chemistry.

Bulletin 107, U.S. Dept. of Agriculture.

Chemical World. Oct. 1913.

Chemical Engineer. April, 1914.

Cohen. Organic Chemistry.


PER CENT LACTIC ACID
TIME IN HOURS
7.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28